



Selective removal of lead from aqueous solutions by ethylenediamine-modified attapulgite

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HIGHLIGHTS

- The sorption ability of attapulgite for lead is largely affected by Na^+ ions.
- Amine modification improves the selectivity of attapulgite for lead removal.
- Uptake mechanism is the chelate interaction between lead and modified sorbent.

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ABSTRACT

The main objective of this work was to explore the feasibility of using ethylenediamine-modified attapulgite (EMATP) as the sorbent for lead removal from water. A novel amine-modified attapulgite was developed, and the structural and surface characteristics of the materials were investigated by N_2 sorption–desorption, Fourier transform infrared (FTIR) spectroscopy, powder X-ray diffraction, zeta potential measurement, and X-ray photoelectron spectroscopy. The amine-modified attapulgite clay extracted from Xuyi, Jiangsu in China exhibited a higher sorption affinity for aqueous $\text{Pb}(\text{II})$ ions resulting from complexation of the metal ions by surface amino groups of the amine-modified attapulgite. Moreover, the sorption affinity for $\text{Pb}(\text{II})$ ions was not affected by the presence of and the alkali metal ions ($\text{Na}(\text{I})$). In addition, ethylenediamine modified attapulgite (EMATP) also has good sorption capacity when incorporating other metal ions ($\text{Cu}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Co}(\text{II})$, and $\text{Ni}(\text{II})$). The sorption kinetic of $\text{Pb}(\text{II})$ was well described by the pseudo-second order kinetic equation while the sorption isotherm followed the Langmuir model. The lead loaded amine-modified attapulgite could be regenerated easily by acid treatment. Findings of the present work highlight the potential use of amine-modified attapulgite as an effective and recyclable sorbent for the selective removal of $\text{Pb}(\text{II})$ ions from water.

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1. Introduction

Nowadays, heavy metal pollution in water remains a serious environmental problem of global concern due to the rapid scientific and technological progress [1]. Lead in particular has been one of the most important pollutants, which arises from lead-storage battery manufacturing factories, the printing industry, pigments used in the dyeing industry, and lead glass manufacturing [2]. Lead poisoning can cause severe damage to the human kidney, nervous system, reproductive system, liver, and brain even at low concentrations [3–5]. Moreover, it is non-biodegradable unlike organic contaminants [6], and tends accumulate in organisms as part of the food chain [7]. Efforts for effective lead removal from water have been continuously made for decades. A variety of technologies, such as chemical precipitation, membrane process, coagula-

tion, phyto-extraction, and electrodialysis, have been applied to the removal of heavy metals from water or the aqueous environment and have been applied with different degrees of success [6]. However, it has been proven that these methods are costly and inept, especially in removing trace amounts of heavy metals [8]. Among available techniques, sorption is widely accepted as a way to remove lead from aqueous solution because the solid sorbents are easy to handle and appropriate for application [9].

Currently, new practices have focused on the use of low-cost natural clay minerals as an alternative to replace conventional sorbents, based on both environmental and economic points of view [10]. Attapulgite clay is abundant in China and about 60% of the attapulgite deposits in China are located in Xuyi County of the Jiangsu Province [11]. It is worth noting that the attapulgite has high viscosity, a large surface area, a moderate layer charge and a large number of silanol groups on its surface, and these physico-chemical characters make it a potentially attractive sorbent for heavy metal ions [4,12–15]. The sorption mechanisms of the heavy

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metals in attapulgite include ion-exchange and adsorption. In theory, ion-exchange and adsorption is nonspecific for the sorption of heavy metal ions. As a result, the alkali metal ions, especially Na^+ , which are ubiquitously present with heavy metals in the water, strongly compete in sorption sites for heavy metals and thus result in a dramatic decrease in sorption capacity of attapulgite [16]. To solve this problem, one of the effective approaches used herein was to develop sorbents of high selectivity toward heavy metal ions by incorporating the functional groups, including carboxylate, hydroxyl, phosphate, amide, and amino groups [17,18]. It is well documented that these heavy metal ions can form complex compounds with amino groups through surface chelation mechanisms; however, attapulgite modified by ethylenediamine had never been tested to see if it had better sorption ability for lead.

In this study, natural attapulgite was activated by dilute hydrochloric acid and further functionalized by ethylenediamine. The physical, chemical, and structural properties of EMATP were characterized by N_2 sorption-desorption, FTIR spectroscopy, X-ray diffraction patterns, zeta potential measurement, and X-ray photoelectron spectroscopy. The sorption characteristics of EMATP for lead removal from aqueous solutions were evaluated in batch experiments. Finally, an attempt was made to explain the mechanism of lead removal using EMATP.

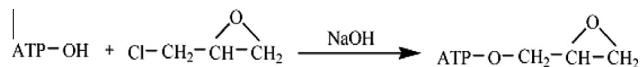
2. Materials and methods

2.1. Materials

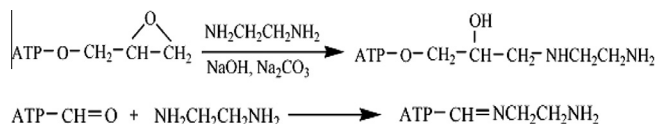
The natural attapulgite used in this work was taken from Xuyi, Jiangsu of China. According to our previous work [19], the natural attapulgite was purified by acid treatment, which was carried out by placing it in contact with 5% HCl with constant stirring for 48 h to remove carbonate and adsorbed cations. It was then filtered, washed with distilled water until neutral, and dried at 110 °C. Then it was manually ground to pass through a 200 mesh sieve. Other chemicals used were of analytical grade and were used without purification. Stock and working solutions of Pb(II) were prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ in 1000 mL volumetric flasks using Milli-Q water, and then diluting to required concentrations. All other solutions were prepared using twice-distilled water.

2.2. Preparation of the ethylenediamine modified attapulgite

Preparation of the ethylenediamine modified attapulgite (EMATP) was similar to methods reported in previous literature [20] with only slight modifications. Ten grams of the acid-treated attapulgite (named as ATP) were mixed with 80 mL of NaOH solution (1.25 mol/L) and 30 mL of epichlorohydrin at 40 °C for 5 h. The mixture was then filtered, rinsed with water many times, oven-dried and stored in a desiccator. During the mixing, the hydroxyl groups of ATP reacted with epichlorohydrin, and the intermediate product was named as epichlorohydrin modified ATP (ECH-ATP). All the proposed chemical equations were referred to in previous literature [20].



Ethylenediamine modified attapulgite (EMATP) was prepared by adding 10 mL ethylenediamine solution, 100 mL water and 1 g NaCO_3 to each 10 g of ATP modified by epichlorohydrin. The mixture was then mixed by agitation at 60 °C for 2 h. EMATP was oven-dried and stored in a desiccator. During this process, the amino groups were grafted on the sorbent.



2.3. Material characterization

Brunauer–Emmett–Teller (BET) surface areas of ATP and EMATP were determined by nitrogen sorption-desorption on a Micrometrics ASAP 2020 analyzer (Micromeritics, USA) at 77 K. Fourier transform infrared (FTIR) spectra of each sample, which was in the form of a KBr disk, were recorded by a FT-IR spectrometer (Nicolet 5700, Thermo Nicolet) to check the changes in the functional groups of materials. The X-ray diffraction (XRD) patterns of the samples were measured in a range of 3–45°. X-ray photoelectron spectroscopy (XPS) (Al K-Alpha, Thermo Fisher Scientific, USA) with monochromatic Al K α X-ray radiation at 1486.71 eV was used to identify the changes of the samples. The zeta potentials of the materials were determined according to [21].

2.4. Batch sorption studies

To prevent precipitation, experiments were carried out at pH < 6.0 to ensure the solubility of Pb(II) ions. The pH values of the solution were adjusted by adding negligible volumes of 0.1 or 0.01 mol/L HNO_3 and/or NaOH solution. After the suspensions were stirred for 24 h, the solid and liquid phases were separated by centrifugation at 10⁴ rpm for 30 min at the same temperature as in the sorption experiments. The Pb(II) content was determined by atomic adsorption spectrophotometer M6 Solaar AAS (Thermo Fisher Scientific, USA).

All experiments were conducted in three runs and the final mean values were used in calculations. The sorption rate (%) and the sorption capacity (q_e) were calculated by the following equations:

$$\text{Sorption rate (\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 and C_e represent the initial and final concentrations (mg/L), respectively. V is the volume of the solution (mL), and m is the sorbent mass (g).

2.5. Desorption and regeneration studies

To evaluate the reusability of EMATP, the desorption of Pb(II) and regeneration of Pb(II) loaded EMATP (Pb-EMATP) were performed in five consecutive cycles [22]. In each cycle, 20 mg/L Pb(II) in 25 mL of solution was mixed with 20 mg EMATP for 24 h at pH 5.0. EMATP were separated and the supernatant was subjected to Pb(II) measurements. The resultant Pb-loaded sorbent was mixed with 10 mL of 1.75 mol/L HNO_3 solution for 10 h. Prior to the next sorption-desorption cycle, regenerated sorbent was washed thoroughly with deionized water until a pH 6.0 was reached.

3. Results and discussion

3.1. Material characterization

The BET surface areas of ATP and EMATP are 136 and 83 m²/g, respectively. The lower surface area of EMATP is probably due to the fact that the surface of ATP is coated by ethylenediamine.

The FTIR spectra of ATP, ECH-EMATP and EMATP are shown in Fig. 1. The main differences in the spectra between ATP and ECH-ATP are the presence of the peaks at about 2924 and 2853 cm^{-1} for aliphatic C–H stretching and the decrease of the peaks at about 3552 cm^{-1} ascribed to the stretching vibrations of –OH, which confirms that the –OH groups of ATP reacts with epichlorohydrin. Compared with the spectrum of ECH-ATP, the main changes of EMATP spectrum are as follows: the peaks at about 2924 and 2853 cm^{-1} and peaks at about 3552 cm^{-1} notably increase, corresponding to the aliphatic C–H stretching and the stretching vibrations of –OH, respectively. Furthermore, new peaks arise at about 3330 and 2963 cm^{-1} ascribed to the N–H stretching bands of ethylenediamine. It indicates that ethylenediamine has been successfully immobilized in ATP and the results are in accordance with the proposed reaction equations.

Fig. 2 shows the XRD patterns of ATP and EMATP. For the XRD spectrum of EMATP, the main peaks are similar to that of ATP, which reveals that the crystal structure of ATP is well maintained after modification.

XPS measurement was performed to characterize the surface compositions of ATP and EMATP (results shown in Table 1). The ATP sample presents an atomic content of 0% for N1s. For EMATP, an N1s peak with atomic content of 6.81% is clearly observed confirming the successful amino-functionalization of the ATP surface.

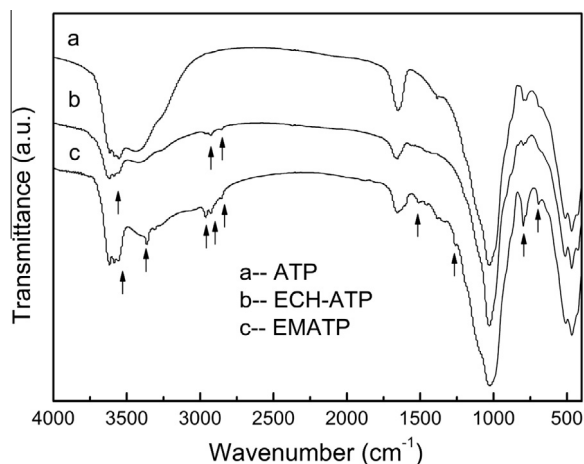


Fig. 1. FTIR spectra of ATP (a), ECH-ATP (b), and EMATP (c).

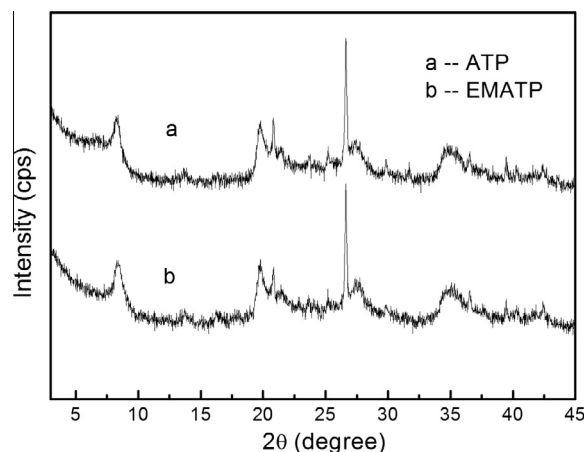


Fig. 2. X-ray diffraction patterns of ATP (a) and EMATP (b).

Table 1

Surface content of C, N, O and Al in ATP and EMATP evaluated by XPS.

Element	XPS surface composition (atom%)	
	ATP	EMATP
C1s	9.61	11.20
N1s	0	6.81
O1s	84.50	76.88
Al2p	5.89	5.11

3.2. Pb(II) sorption studies

3.2.1. Comparison of the sorption properties of Pb(II) onto ATP, ECH-ATP and EMATP

To assess the influence of surface modification, the sorption properties of Pb(II) were tested using ATP, ECH-ATP and EMATP under the following conditions (pH = 4.0, $C_0 = 20 \text{ mg/L}$, $m = 20 \text{ mg}$, $T = 298 \text{ K}$, $V = 25 \text{ mL}$). The results showed that the sorption rates of Pb(II) onto ATP, ECH-ATP and EMATP were 55.5%, 20.1% and 98.4%, respectively. ECH-ATP had the lowest sorption rate of all, probably due to the fact that the effective sorption sites decreased remarkably after epichlorohydrin treatment. In addition, the results indicated that EMATP was the most efficient sorbent to remove Pb(II) from aqueous solution.

3.2.2. Effect of pH

The pH of the sorption medium is an important factor for the sorption of heavy metal ions onto sorbents, because the charge at the sorbent surface and metal ion speciation changes with pH [23]. To investigate the sorption ability of EMATP for Pb(II), the effect of solution pH on the sorption rate of Pb(II) ions onto ATP and EMATP was illustrated in Fig. 3. As observed from Fig. 3, at low pH, the sorption rates of Pb(II) onto ATP and EMATP were both very low, because the high concentration of H^+ competed with Pb(II) in the solution, which was unfavorable for the sorption of Pb(II). In addition, at a pH below about 2.6, EMATP had lower sorption rate than ATP. This was attributed to the fact that most of the amino groups of EMATP were protonated at low pH. The electrostatic repulsion between Pb(II) and the protonated amino groups of EMATP also prevented the sorption of Pb(II) onto EMATP. On the other hand, as pH increased to about 4.0, the sorption rates of Pb(II) onto ATP and EMATP both increased sharply. The increased pH coupled with proton release made sorption more favorable. For EMATP, as pH ranged from about 4.0 to 6.0, the sorption rate of

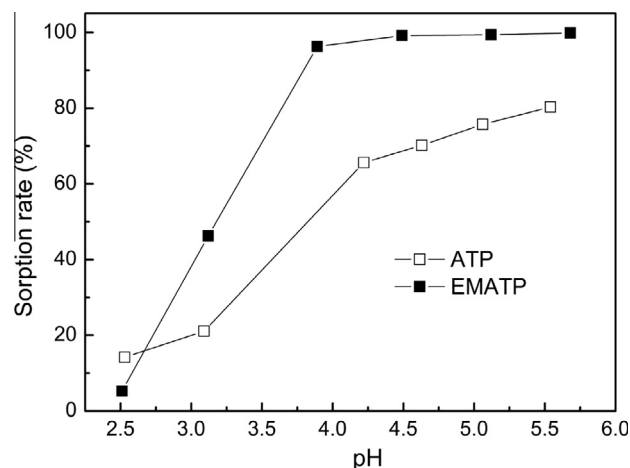


Fig. 3. Effect of pH on the sorption of Pb(II) on ATP and EMATP ($C_0 = 20 \text{ mg/L}$, $T = 298 \text{ K}$, $m = 20 \text{ mg}$, $V = 25 \text{ mL}$).

Pb(II) reached a plateau, probably due to the limitation of saturated sorption capacity of EMATP. Last but not least, EMATP was more efficient for removal of Pb(II) from aqueous solution than ATP.

3.2.3. Effect of coexisting metal ions

The alkali earth metal ions are ubiquitous in natural waters and industrial effluents, so it is important to study the sorption selectivity of EMATP toward target metal ions when assessing its technical applicability [16]. It was reported that Pb(II) sorption by attapulgite was also dominated by the alkali earth ions such as Na^+ ions at higher pH [2]. As reported in the literature [2], the sorption rate of Pb(II) decreased by about 80% when the Na^+ concentration increased from 0.001 mol/L to 0.1 mol/L. Consequently, Na^+ was also chosen as a representative competing cation and its effect on Pb(II) sorption was investigated by exposing Pb(II) to varying concentrations of NaNO_3 (Fig. 4a) in our work. As shown in Fig. 4a, no apparent effect on sorption was observed in the presence of Na^+ under the tested conditions. Compared with the results of the literature [2], EMATP had more selective sorption ability for Pb(II) in the presence of Na^+ ions.

The coexisting heavy metal ions may also affect the sorption of Pb(II). In this section, Cu(II), Zn(II), Mn(II), Cd(II), Co(II), and Ni(II) were chosen as the representative competing cations, and all the metal ions were set at the same concentration. As seen from Fig. 4b, the sorption rate of Pb(II) was greater than that of other ions, which meant that Pb(II) had a priority tendency to be sorbed onto EMATP in solution. This sorption preference for EMATP may be due to the fact that the hydration energy of Pb(II) is lower than those of the other mentioned heavy metal ions [24]. This observation reveals the fact that at trace levels, Pb(II) will be concentrated by the EMATP selectively in the presence of the other mentioned metal ions.

3.2.4. Effect of humic acid

Dissolved humic substances such as humic acid are widespread in the aquatic environment and may affect sorption of Pb(II) onto EMATP. The sorption capacities of Pb(II) onto EMATP in the absence and presence of humic acid were presented in Fig. 5. As shown in Fig. 5, the presence of humic acid slightly decreased the sorption under the tested conditions. That decrease in sorption was likely because the sorption of humic acid components was mainly driven by relatively weak van der Waals forces and electrostatic forces [21,25], which were overwhelmed by the strong complexation interactions between Pb(II) and the amino groups of

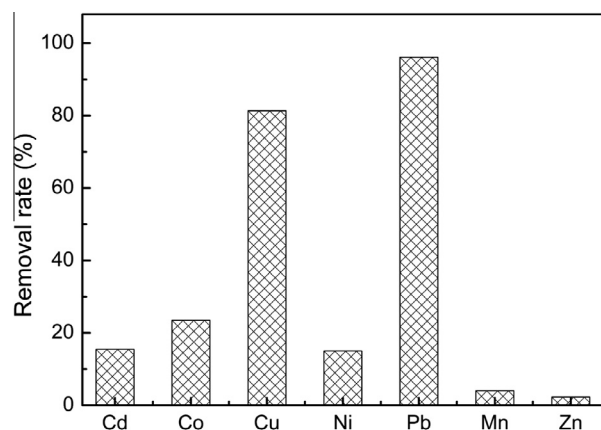


Fig. 4b. Effect of coexisting heavy metal ions on Pb(II) sorption onto EMATP ($C_0 = 20$ mg/L, $T = 298$ K, $m = 100$ mg, $V = 25$ mL, $\text{pH} = 4.0$).

EMATP. All test results indicated that EMATP was potentially a preferable sorbent for the removal of Pb(II).

3.3. Sorption thermodynamics

It is well known that temperature is one of most important parameters which can affect sorption by altering the molecular interactions and the solubility of the sorbate. In engineering practice, entropy and Gibbs free energy factors should be considered in order to determine what process will occur spontaneously.

Thermodynamic parameters such as a change in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) are calculated by the following equations [26]:

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (3)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

where R is the gas constant (8.314 J/(mol K)) and T is the absolute temperature (K). ΔH° and ΔS° are obtained from the slope and intercept at the line plotted by $\ln(q_e/C_e)$ versus $1/T$, respectively.

The obtained thermodynamic parameters for Pb(II) sorption on EMATP were listed in Table 2. The ΔH° values for the sorption of Pb(II) were equal to -12.92 , -8.122 , and -45.34 kJ/mol, respectively. These negative values indicated the exothermic nature of the sorption of Pb(II) onto EMATP in temperature ranges of 27–

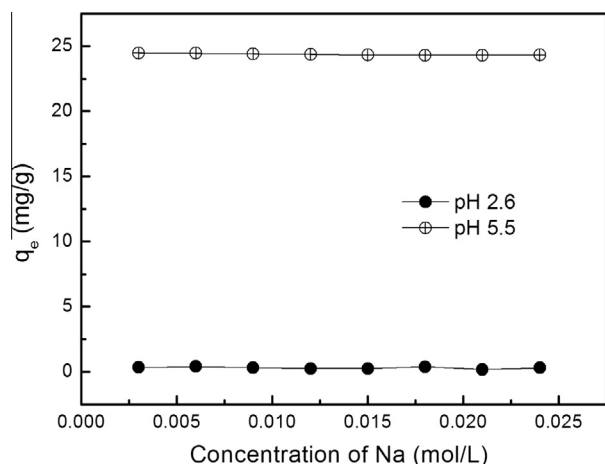


Fig. 4a. Effect of coexisting Na^+ ions on Pb(II) sorption onto EMATP ($C_0 = 20$ mg/L, $T = 298$ K, $m = 20$ mg, $V = 25$ mL).

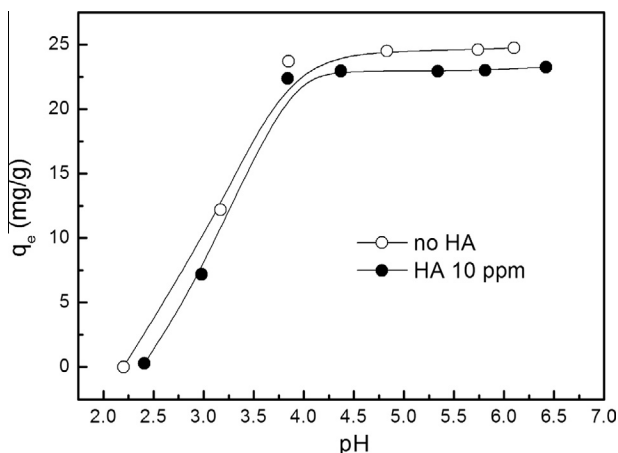


Fig. 5. Effect of HA on the sorption of Pb(II) onto EMATP ($C_0 = 20$ mg/L, $T = 298$ K, $m = 20$ mg, $V = 25$ mL).

Table 2Thermodynamic parameters for Pb(II) sorption onto EMATP (pH = 5.5, $m = 30$ mg, $V = 25$ mL, $C_0 = 20$ mg/L).

C_0 (mg/L)	ΔH (kJ/mol)	ΔS (J/(mol K))	ΔG (kJ/mol)			R^2
			300 (K)	308 (K)	318 (K)	
4	–12.9	–28.9	–4.26	–4.02	–3.74	0.928
40	–8.12	–8.33	–5.62	–5.56	–5.47	0.951
100	–45.3	–129	–6.51	–5.48	–4.18	0.976

45 °C. The values of Gibbs free energy (ΔG°) were calculated directly from Eq. (4). The negative values of ΔG° indicated that the sorption of Pb(II) onto EMATP was thermodynamically feasible and naturally spontaneous at 27–45 °C.

3.4. Sorption isotherms

The sorption isotherms reveal the specific relation between the concentration of sorbate and the sorption capacity of a sorbent at a constant temperature [27]. The Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) sorption isotherms are generally used to describe sorption behavior.

The Langmuir sorption model assumes that sorption occurs at specific homogeneous sites on the sorbent and is the most commonly used model for the monolayer sorption process. Its form can be described by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (5)$$

where q_e is the equilibrium sorption capacity of Pb(II) (mg/g), C_e is the equilibrium concentration of Pb(II) (mg/L), q_m is the maximum Pb(II) sorption capacity (mg/g), and K_L is the Langmuir coefficient relating to the strength of sorption.

The Freundlich sorption model describes the multilayer sorption isotherm for heterogeneous surfaces. The equation is represented by the following equation:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (6)$$

where q_e is the equilibrium sorption capacity of Pb(II) (mg/g), C_e is the equilibrium concentration of Pb(II) (mg/L), and K_F is the Freundlich isotherm constant and $1/n$ (dimensionless) is the heterogeneity factor.

The Dubinin–Radushkevich (D–R) sorption model is generally used to distinguish between physical and chemical sorption [27], given by the following equation:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (7)$$

where q_e is the equilibrium sorption capacity of Pb(II) (mg/g), and β is a constant related to the mean free energy of sorption per mole of the sorbate (mol^2/J^2), and ε is the Polanyi potential, which is equal to $RT \ln(1 + (1/C_e))$, where R (J/(mol K)) is the gas constant and T is the absolute temperature.

The constant β can give valuable information regarding the mean free energy E (kJ/mol) of sorption per molecule of sorbate, and E can be obtained using the following equation [27]:

$$E = \frac{1}{\sqrt{2\beta}} \quad (8)$$

The sorption capacity of Pb(II) onto EMATP, determined as a function of the equilibrium concentration of Pb(II), was shown in Fig. 6. It illustrated that the absolute sorption amount of Pb(II) increased with the increasing of the equilibrium concentration of Pb(II). As shown in Table 3, the correlation coefficient for the Langmuir model was the highest in comparison to values obtained from D–R and Freundlich equations. It indicated that the Langmuir equa-

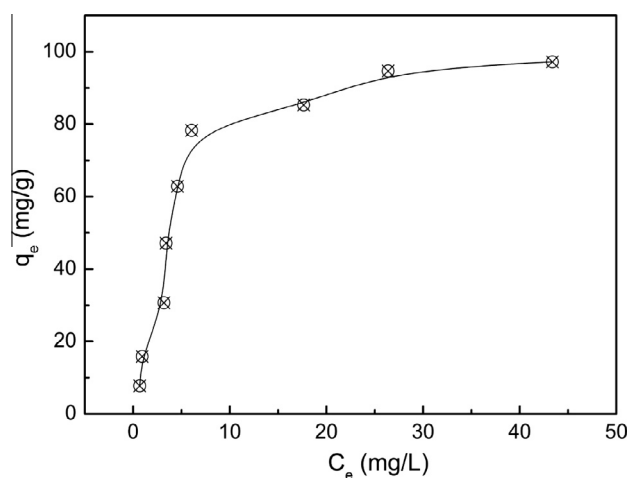


Fig. 6. Sorption isotherm of Pb(II) onto EMATP (pH = 5.0–5.3, $T = 303$ K, $m = 30$ mg, $V = 25$ mL).

tion fitted the sorption isotherm data of Pb(II) onto EMATP well, which was supported by a good correlation coefficient R^2 (0.935) in Table 3. The value of mean free energy E in the D–R model gave information whether the sorption mechanism was chemical sorption, ion exchange, or physical sorption. If E is in the range of 8–16 kJ/mol, the sorption process follows chemical ion exchange. While for $E < 8$ kJ/mol, the sorption process is of a physical nature. For $E > 16$ kJ/mol, the sorption occurs via chemical sorption [28,29]. In this study, the calculated E value was more than 16 kJ/mol indicating that sorption of Pb(II) onto EMATP occurred via chemical sorption.

3.5. Sorption kinetics

To investigate the mechanism of mass transfer process, the pseudo-first-order rate sorption model (Eq. (9)) and pseudo-second-order rate sorption model (Eq. (10)) are commonly used to determine sorption kinetics constants. The sorption models are represented by the following equations:

$$\lg(q_e - q_t) = \lg q_e - K_1 t \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

where q_e and q_t are the amount of Pb(II) sorbed onto the sorbent (mg/g) at equilibrium and at time t (min), respectively. K_1 is the rate constant of pseudo-first-order sorption (1/min), and K_2 is the constant of pseudo-second-order rate (mg/(g min)).

The sorption kinetics data of Pb(II) onto EMATP were shown in Fig. 7a. The fitting parameters and theory data calculated by Eqs. (9) and (10) were listed in Table 4. As seen from Fig. 7a, the sorption of Pb(II) was fast from the beginning of the experiment and thereafter it proceeded at a platform. As shown in Table 4, the correlation coefficient R^2 for the pseudo-first-order sorption model were low. It indicated that the pseudo-first-order sorption model

Table 3
Sorption isotherms parameters for Pb(II) sorption onto EMATP.

Langmuir equation			Freundlich equation			D–R equation		
q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2	q_m (mg/g)	β	R^2
258	5.20×10^{-2}	0.935	3.43	1.76	0.831	128	7.73×10^{-8}	0.912

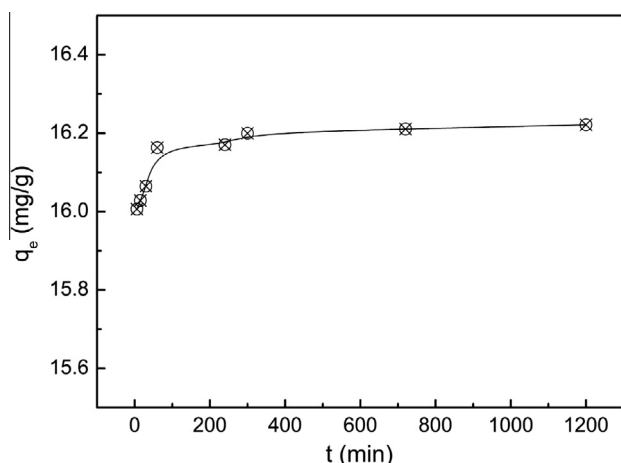


Fig. 7a. Sorption kinetics of Pb(II) onto EMATP ($C_0 = 20$ mg/L, $T = 300$ K, $m = 30$ mg, $V = 25$ mL, $pH = 5.5$).

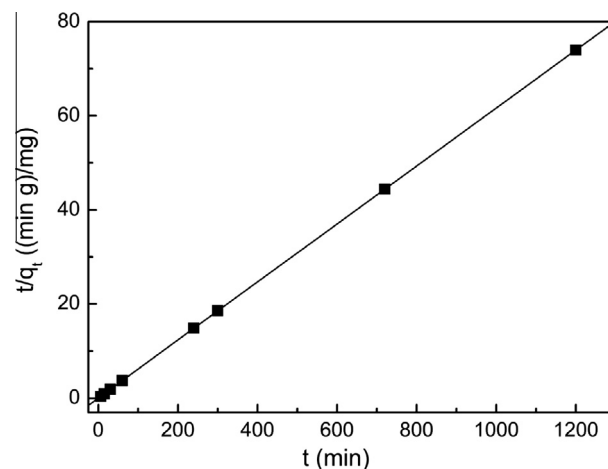


Fig. 7b. Simulation of Pb(II) onto EMATP using pseudo-second-order kinetic model.

was not suitable to fit the experimental data. On the contrary, the value of correlation coefficient R^2 for the pseudo-second-order sorption model was extremely high (approximately 1.00), and the results were supported by Fig. 7b. It suggested that the sorption of Pb(II) onto EMATP followed the pseudo-second-order sorption model, and the chemisorption was the rate controlling mechanism, whose results were fully consistent with those drawn from sorption isotherm analysis as mentioned above [30].

3.6. Sorption mechanism

Zeta potentials of EMATP and EMATP after sorption (Pb-EMATP) were shown in Fig. 8. As seen from Fig. 8, EMATP had permanent negative charges on its surface. After sorption, the negative charges of EMATP decreased in the tested pH range to some extent, but the tendency of zeta potentials was not in accord with that of sorption rate of Pb(II), which suggested the sorption of Pb(II) was not mainly attributed to electrostatic interaction but to the strong complexation interactions between Pb(II) and the amino groups of EMATP.

To better understand the surface chemical characteristics of EMATP and Pb-EMATP, X-ray photoelectron spectroscopy was employed for high resolution spectra (Fig. 9). Deconvolution of the N(1s) spectra yielded three main peaks [19]: peak 1 (399.3 eV), $-\text{NH}$ or $-\text{NH}_2$; peak 2 (400–401 eV), $-\text{N}=\text{}$; and peak 3 (401–402 eV), $-\text{NH}_2^+$ or $-\text{NH}_3^+$. As shown in Fig. 9, compared with the spectrum of EMATP, the significant decrease of N(1s) spectra was verified by peaks at about 399.3 eV. This indicated that Pb(II) interacted with the $-\text{NH}$ or $-\text{NH}_2$ groups through the complexation interactions.

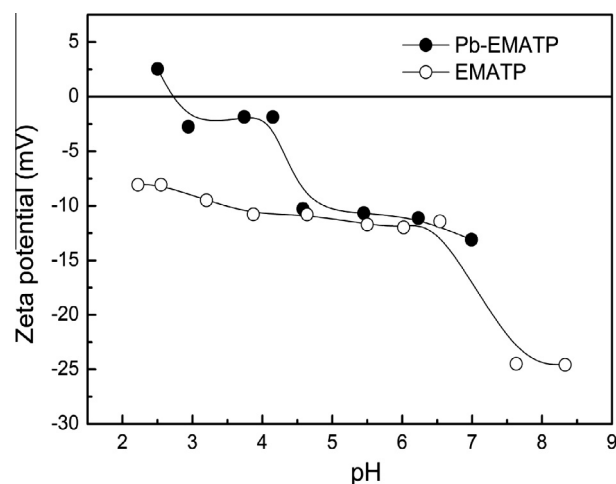


Fig. 8. Zeta potentials of EMATP and Pb-EMATP.

3.7. Regeneration of the sorbent

The regeneration of sorbent is a crucial factor in the practical application of the sorbent. The low sorption capacity of lead onto EMATP at low pH implies that acid treatment may be a feasible approach to regenerating Pb-EMATP. Due to the high stability of EMATP under acidic conditions, Pb-EMATP was regenerated using 1.75 mol/L HNO_3 solution and the regenerated sorbent was reused in sorption in five consecutive cycles. The sorption rate of the regenerated sorbents was illustrated in Fig. 10. The lead sorption

Table 4
Kinetic parameters for Pb(II) sorption onto EMATP.

q_{exp} (mg/g)	Pseudo-first-order equation			Pseudo-second-order equation		
	K_1 (1/min)	q_{cal} (mg/g)	R^2	K_2 (g/(mg min))	q_{cal} (mg/g)	R^2
16.2	9.29×10^{-3}	1.58	0.767	0.188	16.2	1.00

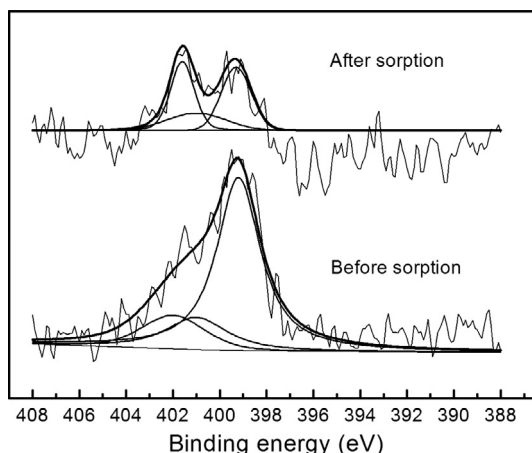


Fig. 9. N(1s) spectra of EMATP before and after sorption.

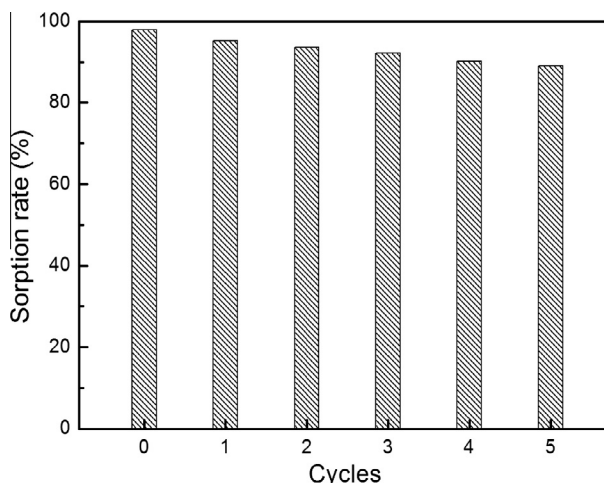


Fig. 10. Pb(II) sorption on EMATP and regenerated EMATP.

capacity of the regenerated EMATP was still maintained at a level of about 90% at the fifth cycle, indicating the high sorption capacities of the sorbents regenerated with acid treatment.

3.8. Test with simulated wastewater

Feasibility of Pb(II) removal by EMATP was demonstrated by applying EMATP to a simulated wastewater. The polluted water sample (25 mL tap water containing 10 mg/L Pb(II)) was found to be Pb(II) free after treated with 0.2 g of EMATP at pH 5.5 for 24 h.

4. Conclusions

In this study, a novel amino-functionalized sorbent (EMATP) was prepared for the sorptive removal of Pb(II) ions from the aqueous solutions. High sorption affinity for aqueous Pb(II) was achieved through the complexation of Pb(II) ions and amino groups on the surface of EMATP. Pb(II) can be concentrated by EMATP selectively in the presence of the above mentioned cations. These unique attributes give EMATP a high potential for effective removal of Pb(II) ions in water treatment.

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References

- [1] O. Ozay, S. Ekici, Y. Baran, N. Aktas, N. Sahiner, Removal of toxic metal ions with magnetic hydrogels, *Water Res.* 43 (2009) 4403–4411.
- [2] Q.H. Fan, Z. Li, H.G. Zhao, Z.H. Jia, J.Z. Xu, W.S. Wu, Sorption of Pb(II) on palygorskite from aqueous solution: effects of pH, ionic strength and temperature, *Appl. Clay Sci.* 45 (2009) 111–116.
- [3] T.K. Naiya, A.K. Bhattacharya, S. Mandal, S.K. Das, The sorption of lead(II) ions on rice husk ash, *J. Hazard. Mater.* 163 (2009) 1254–1264.
- [4] Z. Pei, X. Shan, T. Liu, Y. Xie, B. Wen, S. Zhang, S.U. Khan, Effect of lead on the sorption of 2,4,6-trichlorophenol on soil and peat, *Environ. Pollut.* 147 (2007) 764–770.
- [5] H.Y. Xu, L. Yang, P. Yang, Y. Liu, M.S. Peng, Kinetic research on the sorption of aqueous lead by synthetic carbonate hydroxyapatite, *J. Environ. Manag.* 86 (2008) 319–328.
- [6] M.M. Motsa, B.B. Mamba, J.M. Thwala, T.A.M. Msagati, Preparation, characterization, and application of polypropylene-clinoptilolite composites for the selective adsorption of lead from aqueous media, *J. Colloid Interf. Sci.* 359 (2011) 210–219.
- [7] J.H. Potgieter, S.S. Potgieter-Vermaak, P.D. Kalibantonga, Heavy metals removal from solution by palygorskite clay, *Miner. Eng.* 19 (2006) 463–470.
- [8] C.M. Futralan, C.C. Kan, M.L. Dalida, K.J. Hsien, C. Pascua, M.W. Wan, Comparative and competitive sorption of copper, lead, and nickel using chitosan immobilized on bentonite, *Carbohydr. Polym.* 83 (2011) 528–536.
- [9] Y. Chang, H.i Liu, F. Zha, H. Chen, X. Lei, Adsorption of Pb(II) by N-methylimidazole modified palygorskite, *Chem. Eng. J.* 167 (2011) 183–189.
- [10] A.S. Prado, C. Airolidi, Toxic effect caused on microflora of soil by pesticide picloram application, *J. Environ. Monit.* 3 (2001) 394–397.
- [11] F. Gan, J. Zhou, H. Wang, C. Du, X. Chen, Removal of phosphate from aqueous solution by thermally treated natural palygorskite, *Water Res.* 43 (2009) 2907–2915.
- [12] Q.H. Fan, X.L. Tan, J.X. Li, X.K. Wang, W.S. Wu, G. Montavon, Sorption of Eu(III) on attapulgite studied by batch, XPS, and EXAFS techniques, *Environ. Sci. Technol.* 43 (2009) 5776–5782.
- [13] M. Shirvani, M. Kalbasi, H. Shariatmadari, F. Nourbakhsh, B. Najafi, Sorption-desorption of cadmium in aqueous palygorskite, sepiolite, and calcite suspensions: isotherm hysteresis, *Chemosphere* 65 (2006) 2178–2184.
- [14] Q. Fan, X. Tan, J. Li, X. Wang, W. Wu, G. Montavon, Sorption of Eu(III) on attapulgite studied by batch, XPS, and EXAFS techniques, *Environ. Sci. Technol.* 43 (2009) 5776–5782.
- [15] Q. Fan, D. Shao, Y. Lu, W. Wu, X. Wang, Effect of pH, ionic strength, temperature and humic substances on the sorption of Ni(II) to Na-attapulgite, *Chem. Eng. J.* 150 (2009) 188–195.
- [16] Q. Su, B. Pan, S. Wan, W. Zhang, L. Lv, Use of hydrous manganese dioxide as a potential sorbent for selective removal of lead, cadmium, and zinc ions from water, *J. Colloid Interf. Sci.* 349 (2010) 607–612.
- [17] Y. Chen, B. Pan, H. Li, W. Zhang, L. LV, J. Wu, Selective removal of Cu(II) ions by using cation-exchange resin-supported polyethyleneimine(PEI) nanoclusters, *Environ. Sci. Technol.* 44 (2010) 3508–3513.
- [18] W. Yantasee, Y. Lin, G. Fryxell, Selective removal of copper(II) from aqueous solutions using fine-grained activated carbon functionalized with amine, *Ind. Eng. Chem. Res.* 43 (2004) 2759–2764.
- [19] Y. Deng, F. Wu, B. Liu, X. Hu, C. Sun, Sorptive removal of β -blocker propranolol from aqueous solution by modified attapulgite: effect factors and sorption mechanisms, *Chem. Eng. J.* 174 (2011) 571–578.
- [20] Y. Liu, X. Sun, B. Li, Sorption of Hg^{2+} and Cd^{2+} by ethylenediamine modified peanut shells, *Carbohydr. Polym.* 81 (2010) 335–339.
- [21] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Triblock copolymer syntheses of mesoporous silica with periodic 50–300 Å pores, *Science* 279 (1998) 548–552.
- [22] J. Wang, S. Zheng, Y. Shao, J. Liu, Z. Xu, D. Zhu, Amino-functionalized $Fe_3O_4@SiO_2$ core-shell magnetic nanomaterial as a novel adsorbent for aqueous heavy metals removal, *J. Colloid Interf. Sci.* 349 (2010) 293–299.
- [23] J. Zhang, A. Wang, Sorption of Pb(II) from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgite/sodium humate composite hydrogels, *J. Chem. Eng. Data* 55 (2010) 2379–2384.
- [24] B. Calvo, L. Canoira, F. Morante, J.M. Martínez-Bedia, C. Vinagre, J.E. García-González, J. Elsen, R. Alcantara, Continuous elimination of Pb^{2+} , Cu^{2+} , Zn^{2+} , H^+ and NH_4^+ from acidic waters by ionic exchange on natural zeolites, *J. Hazard. Mater.* 166 (2009) 619–627.
- [25] S. Deng, R.B. Bai, Aminated polyacrylonitrile fibers for humic acid adsorption: behaviors and mechanisms, *Environ. Sci. Technol.* 37 (2003) 5799–5805.
- [26] K.Q. Li, X.H. Wang, Sorptive removal of Pb(II) by activated carbon prepared from *Spartina alterniflora*: equilibrium, kinetics and thermodynamics, *Bioresour. Technol.* 100 (2009) 2810–2815.

- [27] Y. Zheng, J. Zhang, A. Wang, Fast removal of ammonium nitrogen from aqueous solution using chitosan-g-poly(acrylic acid)/attapulgit composite, *Chem. Eng. J.* 155 (2009) 215–222.
- [28] S. Kundu, A.K. Gupta, Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization, *Chem. Eng. J.* 122 (2006) 93–106.
- [29] S. Oh, M.Y. Kwak, W.S. Shin, Competitive sorption of lead and cadmium onto sediments, *Chem. Eng. J.* 152 (2009) 376–388.
- [30] J. Dai, H. Yan, H. Yang, R. Cheng, Simple method for preparation of chitosan/poly(acrylic acid) blending hydrogel beads and adsorption of copper(II) from aqueous solutions, *Chem. Eng. J.* 165 (2010) 240–249.